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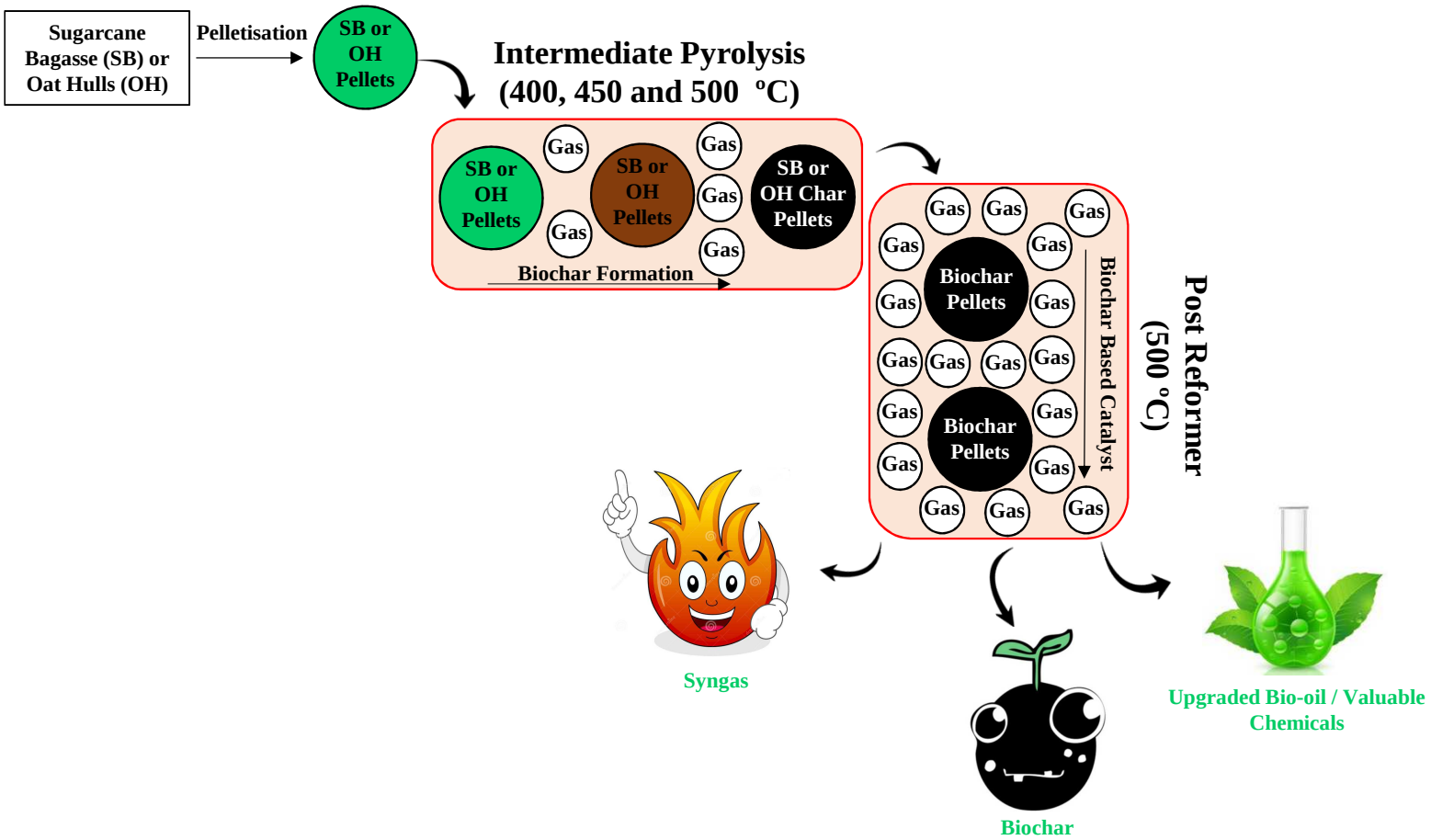
Sugarcane Bagasse (SB) or Oat Hulls (OH)
Pelletisation
SB or OH Pellets
Intermediate Pyrolysis (400, 450 and 500 °C)
SB or OH Pellets
SB or OH Pellets
SB or OH Char Pellets
Gas
Biochar Formation
Biochar Pellets
Biochar Pellets
Biochar Based Catalyst
Post Reformer (500 °C)
Syngas
Biochar
Upgraded Bio-oil / Valuable Chemicals

Valorisation of lignocellulosic biomass investigating different pyrolysis temperatures

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ABSTRACT

Presently, sugarcane bagasse (SB) and oat hulls (OH) have a distinctive potential as a renewable source of biomass, due to its global availability, which is advantageous for producing liquid and gaseous fuels by thermochemical processes. Thermo-Catalytic Reforming (TCR) is a pyrolysis based technology for generating energy vectors (char, bio-oil and syngas) from biomass wastes. This work aims to study the conversion of SB and OH into fuels, using TCR in a 2 kg/h continuous pilot-scale reactor at different pyrolysis temperatures. The pyrolysis temperatures were studied at 400, 450 and 500 ºC, while the subsequent reforming temperature remained constant at 500 ºC. The bio-oil contained the highest calorific value of 33.4 and 33.5 MJ/kg for SB and OH, respectively at 500 ºC pyrolysis temperature, which represented a notable increase compared to the raw material calorific value of SB and OH (16.4 and 16.0 MJ/kg, respectively), this was the result of deoxygenation reactions occurring. Furthermore, the increment of the pyrolysis temperature improved the water content, total acid number (TAN), viscosity and density of the bio-oil. The syngas and the biochar properties did not change significantly with the increase of the pyrolysis temperature. In order to use TCR bio-oil as an engine fuel, it is necessary to carry out some upgrading treatments; or blend it with fossil fuels if it is to be used as a transportation fuel. Overall, TCR is a promising future route for the valorisation of lignocellulosic residues to produce energy vectors.

Keywords: Thermo-Catalytic Reforming; pyrolysis; biofuel; sugarcane bagasse; oat hulls.

Abbreviations: TCR, Thermo-Catalytic Reforming; SB, sugarcane bagasse; OH, oat hulls; CHP, combined heat and power; HHV, higher heating value; PFD, process path flow diagram; TGA, thermo-gravimetric analysis; TCD, thermal conductivity detector; TAN, total acid number; GC-MS, gas chromatography-mass spectrometry.

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1. INTRODUCTION

Concerns over energy demand and security, together with the impact of CO_2 emissions from fossil fuel usage, contributing towards climate change are driving the need to find alternative and sustainable low carbon energy sources [1, 2]. Lignocellulosic agricultural waste is considered one of the most available and cheap green resources for the bioenergy sector and biofuels production [3]. Current methods to

exploit biomass, like extraction of pure cellulose or combustion to generate electricity, are harmful to the environment and not attractive for the industry [4]. In this regard, thermochemical processes (pyrolysis and gasification) are becoming popular in converting biomass into valuable products [5].

Sugarcane is the most prominent farming harvest on the earth and the main residue formed (bagasse) results from the milling of the sugarcane to extract its juice for ethanol or sugar production [6]. Sugarcane bagasse (SB) is a raw material available worldwide generated in 115 countries (such as USA, India, Australia, Brazil and others) and its production is more significant and more efficient in tropical and sub-tropical climates [7]. SB components are dispersed in a lamella structure, and their composition is around 40-50% cellulose, 20-30% hemicellulose, 20-25% lignin and 1.5-3% ash [6]. The SB cellulose contains amorphous and crystalline components which need to be submitted to physical and thermochemical treatments to have access to the polysaccharides elements [8]. Milling is a suitable example of a physical process to raise the particle surface area of the SB. Thermochemical treatments such as acid reagents, ammonia, steam explosion and alkaline hydroxide have been described to convert SB crystalline components into polysaccharide elements [9-11].

Currently, oat is one of the most produced cereals in the world, and its hulls (residue from oat milling process) have unique potential as a renewable source of biomass due to its global and annual availability. Oat hulls (OH) can be a promising feedstock to produce liquid and gaseous fuels through thermochemical processes (pyrolysis and gasification) [12]. The composition of OH is cellulose (35-45%), hemicellulose (32-35%) and lignin (17-20%) and the hull represents between 20% and 35% of the entire grain weight [13]. One of its advantages is the low ash content (between 4.5% and 5.2%) and the homogenous morphologic and particle size that does not need to be milled when treated [13].

Pyrolysis processes are categorised into slow, intermediate and fast [14, 15]. Each implements different heating rates, temperatures and vapour/solid residence times to the feedstock. However, a standard parameter is that heating of the feedstock always occurs under starved or oxygen-free atmospheres. Every type of pyrolysis process produces the same products (bio-oil, biochar and syngas), which are highly variable depending on the pyrolysis technique applied [16]. Slow pyrolysis involves low heating rates, long solid residence times and the main product is char. Fast pyrolysis applies high heating rates, short vapour residence times and yields higher quantities of liquids (up to 75 wt% on a dry basis) [16]. Intermediate pyrolysis occurs at temperatures between 400 to 500 ºC, solid heating rates (minutes/ºC), solid residence times (minutes), with a short vapour residence time (seconds) and produces relatively equal yields of all products, solids, liquids and gases [17]. Slow and intermediate pyrolysis is the most suitable techniques to produce biochar, but intermediate pyrolysis offers shorter solid residence times [18].

Moreover, slow pyrolysis is a process mostly used for char formation, and it is rarely seen to produce a reasonable yield of bio-oil (mainly tars formed) or to be associated with combustion to generate heat and power [19]. The most relevant variation between fast and intermediate technologies is the solid residence times, causing a different heat transfer to the biomass. It leads to better control of the chemical reactions and a lower thermal cracking of the bio-components, resulting in less tar formation and general optimisation of the products formed [5]. Pyrolysis oil from the intermediate process contains less viscosity, tars and ashes (lower contamination level) leading to phase separation (organic and aqueous phases) and it is easier to separate the organic phase from the aqueous phase, in comparison with fast pyrolysis where little

phase separation occurs [19, 20]. Depending on the feedstock and process parameters applied, intermediate pyrolysis can yield energy vectors with improved physical and chemical properties [17]. The intermediate process is capable of converting large materials (chips, pellets and briquettes) and also fine particles down to dust (from shredding, grinding and chopping) with higher moisture contents when compared to other pyrolysis technologies [18]. Intermediate pyrolysis can process a varied range of materials such as industrial residues, sewage sludge, organic waste, algae, digestate, forest residues, grass, de-inking sludge and agricultural waste [21, 22].

Thermo-Catalytic Reforming (TCR) technology is a combination of intermediate pyrolysis and post catalytic treatment (reforming). It was developed and implemented by Fraunhofer UMSICHT, and it belongs to a bio-battery model used to provide energy from renewable materials [17]. This process contains intermediate pyrolysis section (biochar is being made by heating the biomass in the absence of oxygen) and reforming section (biochar is collected which was formed from the pyrolysis section). In the reforming section, the catalytic cracking of pyrolysis vapours using biochar as a catalyst takes place at high temperatures between 500 to 700 ºC to promote the formation of synthesis gas and organic vapours which when condensed yield bio-oil with superior physicochemical properties [23-25]. The gas exiting the reactor is partially condensed, generating three different products: an organic bio-oil (6-11%), an aqueous phase (21-35%) and a syngas fraction (27-44%).

The overall goal of this work was to study lignocellulosic biomass conversion into upgraded fuels, using TCR technology. However, a comparison of different pyrolysis temperatures of SB and OH has never been investigated in the TCR technology. In this research, we report the impact of different pyrolysis temperatures (400, 450 and 500 ºC) at constant reforming temperature (500 ºC) which are proposed to convert SB and OH into bio-oil, syngas and biochar using a laboratory-scale TCR reactor (2 kg/h).

2. MATERIALS AND METHODS

2.1 Raw Materials

SB (6 wt% moisture content) used in the TCR experiment was supplied from Cosan Biomassa S/A (Brazil) and OH (14 wt% moisture content) was provided by Miller Ltd (UK). Both feedstocks were received with a moisture content <15 wt%. Therefore, no drying was required before the thermal conversion. Pelletisation was performed to ensure consistency homogeneity of the raw SB and OH throughout the TCR process remained the same and to facilitate with the transport of the material through the reactor. Pelletisation was done using a KKP 300 F (22 kWe) motorised pelletiser with a total capacity of 300 kg/h throughput (pellets formed were 6 mm diameter by 23 mm length). Prior to pelletising, the feedstock was analysed in order to determine the proximate, ultimate compositions and higher heating value (HHV).

2.2 TCR Experimental Procedure

The TCR bench-scale reactor was constructed, installed and commissioned at the laboratory of Fraunhofer UMSICHT Institute, Germany with a capacity to process up to 2 kg/h of biomass. The process flow diagram (PFD) of the TCR technology is shown in **Figure 1**.

Before the experiment, the auger screw reactor was gradually heated for 80 minutes to 200 ºC in heating zone 1 (to evaporate light volatile compounds) and between 400 and 500 ºC in the second and third zones (for intermediate pyrolysis reactions) this occurred before the introduction of feedstock into the post reformer. In

the post reformer stage, the temperatures remained constant at 500 ºC. During the heating process, the rotating screws were also turned on, and the speeds of the inner and outer screws were 4 rpm and 1.25 rpm, respectively.

Once the TCR had reached steady-state temperature, the first screw in the auger reactor was stopped, and the sealed hopper was opened to feed the plant with 3.5 kg of pelletised biomass (SB or OH). Then, the feed hopper was closed, and the unit was flushed with N_2 again to decrease the oxygen below to 0.5%. When the N_2 flow was stopped, the first screw in the auger reactor was turned on initiating the introduction of biomass into the TCR unit at a rate of up to 1.4 kg/h. The solid residence time was estimated to be between 5 and 10 minutes.

The post reformer collected the produced char from the previous step. In the post reformer, the catalytic effect which is caused by the reactions between the biochar and the pyrolysis vapours converts the non-condensable gases into a syngas rich in H_2 or CH_4 and condensable gases into upgraded bio-oil. During the reforming process, the condensable organic vapours were upgraded using biochar as a catalyst, enhancing their chemical and physical fuel properties.

Subsequently, upgraded organic vapours were quenched at -5 ºC in the condensing unit to guarantee a complete separation between the pyrolysis liquid and the gas fraction. The bio-oil formed was collected and stored every thirty minutes in an external vessel. Then, the remaining non-condensable vapours passed through the filtration unit for aerosols, fine particles and other contaminants removal. The cleaned gas was directly measured and analysed via an online gas analyser/calorimeter.

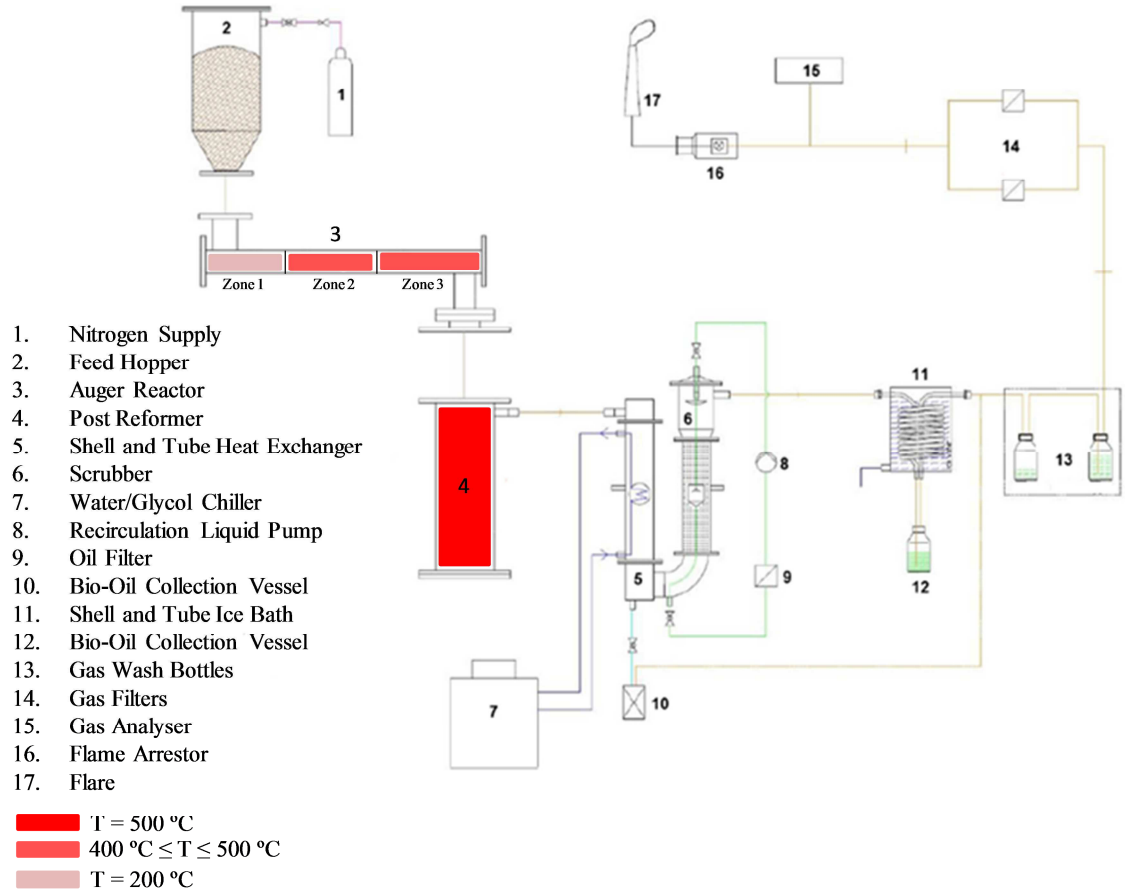

Figure 1. TCR (2 kg/h) process path flow diagram (PFD) [23].

2.3 Proximate Analysis

Total moisture content was determined by drying the sample at 105 ± 3 ºC in a muffle furnace (Philips K5 94) with an inert atmosphere for 3 h. The percentage of moisture was calculated based on the amount of mass loss, according to ASTM E1756-08. The ash content was measured using the same muffle furnace at 575 ± 25 ºC, in which the ash content was determined by the calculation from the mass of the residue remaining after the sample was heated in the air under rigidly controlled conditions of time (according to ASTM E1755-01). Volatiles and fixed carbon were determined by thermo-gravimetric analysis (TGA) technique (NETZSCH TG 209 F1 IRIS). Approximately 15 mg of dried feedstock was inserted into a crucible and pyrolysed under an inert atmosphere of nitrogen at a flow rate of 60 ml/min, to a maximum temperature of 900 ± 10 ºC, with a heating rate of 10 ºC/min and holding time of 15 minutes (according to BS EN 15148:2009).

2.4 Ultimate Analysis

Prepared samples were sent to an external laboratory (MEDAC Ltd) for CHNS analysis (with oxygen determined by difference). The CHN analysis was carried out according to ASTM E777 and ASTM E778. The sulphur content was measured according to ASTM E775. The original analytical method (using the Thermo FlashEA® 1112 Elemental Analyser) was based on the complete and instantaneous oxidation of the sample by "flash combustion" which converts all organic and inorganic substances into combustion products. The resulting combustion gases passed through a reduction furnace and were swept into the chromatographic column (CHNS/NCS separation column, 2 m, 6x5 mm PTFE) by the carrier gas (He). The combustion gases were separated and detected by a thermal conductivity detector (automatic EAGER300™), which gave an output signal proportional to the concentration of the individual components of the mixture.

2.5 HHV

The HHV (MJ/kg) was determined using the unified correlation for fuels developed by Channiwala et al. [26]. The C, H, S, O, N and A are carbon weight fraction, hydrogen, sulphur, oxygen, nitrogen and ash, respectively:

$$HHV\ (MJ/kg) = 0.3491\ (C) + 1.1783\ (H) + 0.1005\ (S) - 0.1034\ (O) - 0.0151\ (N) - 0.0211\ (A). \quad \text{(Equation 1)}$$

2.6 Products Characterisation

After the experiment, the produced liquid was separated by gravity (using a separating funnel) into two phases with different densities: an organic oil phase at the top and an aqueous phase at the bottom. Then, the pyrolysis liquid was analysed to determine the chemical and physical properties. Biochar and syngas were also characterised.

2.6.1 Oil and char ultimate analyses

Pyrolysis liquid and char samples were analysed externally at MEDAC Ltd, applying the same method as in section 2.4 for the determination of the elemental compositions (C, H, N, O and S). Furthermore, the oxygen was determined by the difference ($100 - \sum$ (CHNS + ash)).

2.6.2 Oil and char ash contents

The ash content of the oil was calculated in accordance with ASTM D482. The carbonaceous solid samples produced from the carbon residue test were combusted in a muffle furnace at 775 ºC. The remaining ash was cooled at room temperature and weighed, then expressed as a mass percentage of the original oil sample. The ash of the char was determined in a muffle furnace at 575 ºC, described in section 2.3 according to ASTM E1755-01.

2.6.3 HHV

The HHV of the bio-oil and char was determined using the unified correlation for fuels as described in section 2.5.

2.6.4 Water content

The water content of the bio-oil was determined using a Mettler Toledo V30 compact volumetric Karl Fischer titration in accordance with ASTM E203-01. The result was corrected to the weight percent of the total sample.

2.6.5 Total acid number (TAN)

The TAN of the oil was determined with a Mettler Toledo V20 compact titrator using the potentiometric titration method in accordance with ASTM D664. The oil sample was dissolved in a 50/50 toluene and isopropanol solution and titrated potentiometrically with 0.1 N alcoholic potassium hydroxide using a combination electrode. Readings were automatically plotted against the volume of the titrating KOH solution used until the titration endpoint was achieved.

2.6.6 Viscosity

Viscosity was determined with a Cannon–Fenske Routine glass capillary viscometer (ASTM D445). Throughout the analysis, the viscometer was setting at 40 ºC allowing passage of a specific pyrolysis oil quantity over the capillary. The final viscosity is the multiplication of the oil travelling time (registered before) and the viscometer constant.

2.6.7 Density

The pyrolysis oil density was measured at 22 ºC using a glass hydrometer in the range (0.8–1.0 g/cm^3), according to ASTM D1298.

2.6.8 Gas chromatography-mass spectrometry (liquid-GC-MS)

The bio-oil sample was analysed with GC-MS apparatus equipped with a polar chromatographic column. The polar analysis was performed with a 7820A Agilent HP gas chromatograph connected to a 5977E Agilent HP quadrupole mass spectrometer (EI 70 eV, at a frequency of 1.55 scan/s within the 29-300 *m/z* range). Analytes were separated by a nitroterephthalic acid-modified polyethylene glycol DB-FFAP (30 m, 0.25 mm ID, 0.2 μm film thickness) column using helium as a carrier gas with the following thermal program: 50 ºC with a hold for 5 minutes; then ramping up with a heating rate of 10 ºC/min until 250 ºC; followed by column cleaning at 250 ºC for 10 minutes. A sample of bio-oil was dissolved in acetonitrile solution to a 1% (w/v concentration), spiked with 0.1 ml internal standard solution (1000 mg/l, 2-ethyl butyric acid in acetonitrile). The compounds were identified by library searches (NIST libraries). The mass spectra evaluation was quantified in terms of relative abundance of peak area (% is the individual peak area to the total area).

2.6.9 Gas analysis

The produced pyrolysis gas was frequently measured and analysed using a gas analyser MGA 12, Dr Födisch Umweltmesstechnik, according to EN 15267-3 standard test procedure. The measurement principle of the gas analyser is based on an infrared photometer (CO, CO_2 and CH_4), an electrochemical cell (O_2) and a TCD (H_2). The heating value of the gas phase was quantified using the Union Instruments CWD2005 process gas analyser. The calibration of the gas analysers was performed prior to the experiments.

3. RESULTS AND DISCUSSION

3.1 Feedstock Characterisation

Table 1 shows the proximate and ultimate analyses of the lignocellulosic residues (raw SB and OH). The SB characterisation values of the current work do not present a close correlation when compared to the literature [4, 6, 27, 28]. There are more than 500 sugarcane species, and their chemical composition can be slightly different [28]. Only the ash (3.1 wt%), water (5.4 wt%) and the elemental composition (44.9 wt% of carbon, 5.9 wt% of hydrogen and 45.8 wt% of oxygen) found in Varma et al. [6] study were similar to this study. Al Arni [27] investigated bagasse with moisture, ash content and HHV of 8.5, 5.9 wt% and 18.2 MJ/kg, respectively.

The OH characterisation values are compared with the literature results [29-31]. Abedi et al. [29] reported for the same type of biomass 41.8, 6.4, 44.7 wt% and 16.8 MJ/kg for C, H, O and HHV, respectively. However, the same study showed a lower level of moisture (8.5 wt.%) and a higher amount of ash (5.8 wt.%), which is a disadvantage for char production and their respective properties [32]. Zhang et al. [31] calculated the elemental composition (C, H and O) and HHV for OH obtaining 43.5, 4.7, 45.9 wt% and 16.1 MJ/kg, respectively.

Table 1. Feedstock characterisation.

	SB	**OH**
Ultimate analysis (moisture-free basis)		
C (wt%)	43.7	40.6
H (wt%)	5.1	6.0
N (wt%)	0.1	1.1
S (wt%)	0.6	<0.1
O (wt%)	46.5	49.9
Proximate analysis (dry basis)		
Moisture (wt%)	6.0	14.8
Ash (wt%)	4.0	2.4
Fixed carbon (wt%)	17.2	26.4
Volatiles (wt%)	72.8	56.4
HHV (MJ/kg)	16.4	16.0

3.2 Bio-liquids Analyses

Table 2 shows the chemical composition and fuel properties of the SB and OH bio-oils applying different pyrolysis temperatures in the reactor. The levels of nitrogen and sulphur (<2 wt% and <1.4 wt%, respectively) are acceptable if the purpose of the SB and OH bio-oils is to be burned or combusted as a fuel [33]. The sulphur and nitrogen contents should be about 500 and 148 ppm for diesel engine fuels [34, 35]. Additionally, low NO_x and SO_x emissions are preferable for environmental reasons [33].

The ash content revealed was extremely low (<0.001%), which is positive for engine applications as this minimises corrosion, blocking and deposition of sediments during its operation [36]. Based on the ash content of all SB and OH oils, it is evident that TCR technology can produce a bio-oil containing very low residues of ash which is attractive as a fuel.

SB and OH oils present lower acidity when submitted to higher pyrolysis temperatures. The total acid number (TAN) of SB and OH decreased from 32.2 to 25.8 mg KOH/g and from 33.5 to 24.2 mg KOH/g with increasing the pyrolysis temperature from 400 to 500 ºC, respectively. The acid number of this work is significantly higher in comparison with diesel (0.24 mg KOH/g) [37] and biodiesel (0.8 mg KOH/g) [38]. However, Asadullah et al. [39] reported that fast pyrolysis of sugarcane bagasse from the fixed bed reactor at temperatures of 500 ºC has much higher acid content (137.35 mg KOH/g*)* in comparison with this study (25.8-32.2 mg KOH/g). These values are still high for engines, but it is essential to highlight the role of TCR in producing a bio-oil with lower acidity.

In terms of viscosity, higher pyrolysis temperatures were more effective in cracking the organic vapours, thus forming lighter weight molecules and reducing the viscosity of the bio-oil. The viscosity improved from 47.8 to 23.7 mm^2/s for SB and from 38.1 to 35.3 mm^2/s for OH with increasing the pyrolysis temperatures. This is an advantage to improve the fuel flow of the engine causing better combustion, despite the results are still considered high for engine applications [40].

Higher pyrolysis temperatures were able to produce lighter chemical compounds which reduced the density of the pyrolysis liquid. Lower density influences the injection time and the consumption rate, which improves the engine performance [41].

Higher pyrolysis temperatures decreased the amount of moisture which improves the HHV and the properties of the oil in terms of engine performance [22]. The rise in the pyrolysis temperature also helped in the promotion of dehydration reactions reducing the percentage of water.

An increment of the pyrolysis temperature led to a bio-oil with less oxygen and more carbon for both feedstocks. As a consequence, TCR bio-oil contained a better HHV with higher pyrolysis temperatures. It is reasonable to conclude that higher pyrolysis temperatures might stimulate more depolymerisation and thermal breaking reactions of hemicellulose and cellulose resulting in a bio-oil with less oxygen, more carbon and a higher calorific value [42]. Varying the pyrolysis temperature resulted in a bio-oil HHV between 29.1 and 33.5 MJ/kg for both feedstocks. The bio-oil contained the highest calorific value of 33.4 MJ/kg from SB and 33.5 MJ/kg from OH at 500 ºC pyrolysis temperature. The SB and OH experiments produced a pyrolysis oil with better energy density attributed to the higher carbon and lower oxygen content.

Varma et al. [6] and Treedet et al. [43] converted SB through fast pyrolysis at 500 ºC using a semi-batch and fluidised bed reactors, respectively. In both cases, the HHV of the bio-oil (27.7 and 18.4 MJ/kg) was lower compared to the SB runs of the present work. Treedet et al. [43] also produced SB pyrolysis oil with a higher percentage of water (38.9 wt%) and higher density (1259 kg/m^3) than this set of experiments.

Results show an improvement of the bio-oil HHV when increased the pyrolysis temperature. Surprisingly, Henkel et al. [44] had precisely the opposite trend processing SB in an intermediate pyrolysis batch reactor. However, this study changed the pyrolysis temperatures from 500 to 700 ºC and not between 400 and 500 ºC, which might be the main cause for the decrease of the calorific value of the bio-oil. It is well

known that cellulose and hemicellulose depolymerisation reactions are more active between 400 and 500 ºC, influencing the characteristics of the pyrolysis oil [45].

The SB oil at 400 ºC of the present work revealed better results than Ahmad et al. [46] with the same biomass and experimental conditions. The difference between both studies can be explained by the existence of many species of SB which might have diverse chemical compositions. Ahmad et al. [46] produced a bio-oil with higher oxygen content (35.2 wt%) and water (25.6 wt%), and lower carbon value (53.7 wt%) and HHV (24.3 MJ/kg).

The heating value of TCR bio-oil from SB and OH (33.4 and 33.5 MJ/K, respectively) at 500 ºC pyrolysis temperature slightly different from biodiesel heating value (37.10 MJ/kg) [47] and they are lower than fossil-based diesel (42 MJ/kg) [48]. The difference between diesel and pyrolysis oil is related to the high oxygen content of biomass-derived fuels due to the presence of complex compounds such as ethers, ketones, aldehydes, acids and carbolic groups [49]. The oxygen content of SB and OH at 500 ºC pyrolysis temperature was approximately 15 times higher than the diesel (1.0 wt%) [48].

The Van Krevelen diagram is shown in **Figure 2,** which represents the O/C and H/C ratios for different technologies. The TCR results are selected at 400 ºC reactor and 500 ºC reforming temperatures which contain the highest oxygen content for SB and OH bio-oils. The O/C ratios of SB and OH bio-oils were 0.32 and 0.18, respectively. The H/C ratios of SB and OH bio-oils were 1.57 and 1.45, respectively. However, the bio-oil from fast pyrolysis of lignocellulosic biomass has much higher values of O/C (0.76) and H/C (1.72) [50] than the results from TCR of SB and OH. Moreover, the O/C and H/C ratios of TCR of OH result is slightly different from hydrotreated bio-oil from switchgrass [51]. Therefore, the molar ratio of O/C and H/C of SB and OH shows significant improvement in bio-oil stability and performance characteristics in comparison to other technologies. The TCR bio-oil of SB and OH have higher calorific value, lower oxygen and viscosity contents at 500 ºC pyrolysis temperature in comparison with other pyrolysis temperatures (400 ºC and 45 ºC) in this study.

The aqueous phase fraction of TCR contained high oxygen content in comparison with TCR bio-oil [24, 52]. The aqueous phase of sugarcane bagasse showed lower oxygen content in the absence of the reforming unit in TCR process, thus suggesting the probability of higher energy content in the aqueous phase fraction [46]. The aqueous phase of TCR contains a mixture of oxygenated compounds including water, carboxylic acids, ketones, phenols, aldehydes, sugars and furans [52]. The application of the aqueous phase from TCR process should be considered since the aqueous phase accounts for 25-35 wt% of overall mass balance. The hydrogen content can be increased by the injection of steam/aqueous phase of TCR into the process that enhances water gas shift reaction [23, 53]. TCR process separated the bio-oil and the aqueous phase. However, the fast pyrolysis unit produced a mixture of bio-oil and the aqueous phase thus requires an external source of hydrogen to upgrade the bio-oil [54, 55]. Tsai et al. reported that fast pyrolysis of sugarcane bagasse at 500 ºC produced between 23-47 wt% of total liquids which is a mixture of both (water phase and organic phase liquids) with the calorific value of 5.12 MJ/kg [56]. Furthermore, promising research have studied that the bio-oil aqueous phase can be applied in a wide range of applications such as composting, crop pest control, crop growth promotion, feed additives, deodorising, coagulating and antifungal agents [57, 58].

In conclusion, the bio-oil of SB and OH from TCR process have superior physical and chemical fuel properties compared to other technologies. The bio-oil can be separated easily from the aqueous phase in TCR process, which is opposite of fast

pyrolysis bio-oil [16, 17]. The TCR crude-oil from SB and OH showed some positive aspects to be used as fuel for engines when compared to other pyrolysis technologies. It is demonstrated sufficient quality to be burned in combustors, boilers and CHP engines or similar applications [17]. In order to use the TCR bio-oil in an engine fuel, it is necessary to blend it with fossil fuels or carry out hydrotreatment upgrading. There is no need for an external source of hydrogen as it can be produced from the TCR unit and can be improved by injection of TCR aqueous phase into the system. Therefore, further study engine tests need to be done to use TCR bio-oils of SB and OH as transportation fuels.

Table 2. SB and OH bio-oil characterisation at different pyrolysis temperatures (reforming temperature = 500 ºC).

	SB			**OH**		
Pyrolysis Temperature (ºC)	**400**	**450**	**500**	**400**	**450**	**500**
Ultimate analysis						
C (wt%)	63.4	71.3	72.2	70.7	72.2	72.8
H (wt%)	8.3	7.1	8.6	8.6	8.2	8.3
N (wt%)	0.4	0.7	0.7	1.8	1.9	1.8
S (wt%)	0.4	0.1	0.3	1.3	0.7	0.7
O (wt%)	27.5	20.8	18.2	17.6	17.0	16.4
Fuel properties						
HHV (MJ/kg)	29.1	31.1	33.4	33.1	33.2	33.5
Ash (wt%)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Water (wt%)	9.9	4.7	4.2	7.8	4.8	4.4
TAN (mg KOH/g)	32.2	27.7	25.8	33.5	30.5	24.2
Viscosity (mm^2/s)	47.8	24.9	23.7	38.1	36.5	35.3
Density (kg/m^3)	1077	1062	1061	1078	1074	1072

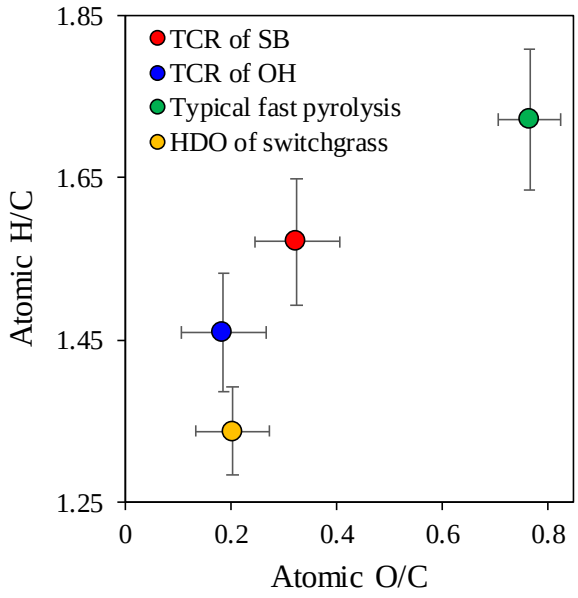

Figure 2. The Van Krevelen diagram of TCR of SB and OH bio-oil (at 400 ºC reactor temperature and 500 ºC reforming temperature) and fast pyrolysis bio-oil from lignocellulosic biomass [50], as well as, hydrotreated bio-oil from switchgrass [51].

3.3 GC-MS Analysis of Bio-oil

The 14 most relevant and frequent peaks were identified, as shown in **Figures S1** and **S2.** The GC-MS results are represented in **Table 3** for SB and OH bio-oil (organic fraction) at different pyrolysis temperatures. Phenols, aromatics and furans are the most common chemical compounds present in the SB and OH bio-oils. For both feedstocks, phenols represent the main group in the bio-oil, which is responsible for the high acidity found in **Table 2** [19].

Phenols and aromatics were the highest fractions of bi-oil, but furans were the less abundant compound. Furans are derived from hemicellulose, while phenols are formed from lignin, and their presence in TCR liquids showed that both fractions were thermally degraded during the process efficiently [59, 60]. When the pyrolysis temperature was at 500 ºC, the benzene and toluene yields were higher in comparison with other pyrolysis temperatures. High pyrolysis temperatures have a significant effect on the stimulation of deoxygenation reactions increasing the level of aromatics present in the pyrolysis liquid [61].

Table 3. Compounds detected and identified by GC-MS of the SB and OH bio-oil at different pyrolysis temperatures (reforming temperature = 500 ºC).

			SB			**OH**		
	Pyrolysis Temperature (ºC)		**400**	**450**	**500**	**400**	**450**	**500**
#	Group	Chemical compound	Conc. (%)			Conc. (%)		
1	Aromatic	Benzene	4.77	5.76	5.29	5.88	5.71	6.51
2	Aromatic	Toluene	5.63	7.06	6.99	8.38	7.98	9.61
3	Furan	Furfural	6.73	6.56	5.29	5.48	5.71	4.4
4	Furan	2-Furanmethanol	4.70	4.55	3.78	5.58	5.98	4.74

5	Aromatic	Ethylbenzene	4.71	5.00	4.11	6.28	5.42	6.31
6	Aromatic	Benzene, 1,3-dimethyl-	4.91	5.16	4.69	5.11	5.49	5.21
7	Aromatic	1,3,5,7-Cyclooctatetraene	4.95	5.66	5.49	7.58	5.98	8.21
8	Phenol	Phenol	10.33	10.26	11.79	10.28	10.48	10.31
9	Phenol	Phenol, 2-methyl-	6.83	7.46	8.09	7.68	7.78	8.01
10	Phenol	Phenol, 3-methyl-	9.83	9.76	11.49	8.98	9.48	10.21
11	Phenol	Phenol, 2,4-dimethyl-	5.43	5.46	4.79	5.00	5.88	5.41
12	Phenol	Phenol, 4-ethyl-	17.73	11.96	11.39	8.98	10.98	8.41
13	Aromatic	Naphthalene	5.21	6.25	6.49	8.38	6.18	6.31
14	Furan	Benzofuran, 2,3-dihydro-	8.24	9.10	10.32	6.41	6.95	6.35

3.4 Gas Analysis

The gas composition (H_2, CH_4, CO, CO_2 and C_XH_Y) of the SB and OH experiments at different pyrolysis temperatures are shown in **Table 4**. The non-detectable volume in the syngas might be the existence of hydrocarbons like ethylene and propane not detected by the gas analyser. Applying 400 and 450 ºC as pyrolysis temperature, CO_2 was the main gas in SB and OH syngas. Low pyrolysis temperatures stimulate the degradation of hemicellulose and cellulose, which is linked to the cracking of carboxyl and carbonyl compounds, increasing the formation of CO_2 [62].

When the pyrolysis temperature is raised, the volume of CO_2 decreased for the reasons mentioned previously, related to the decomposition of cellulose and hemicellulose. Methane yields were also reduced with the increment of pyrolysis temperature due to lignin deformation at different pyrolysis temperatures [45]. It is reported that lignin deformation and cracking released much more H_2 and CH_4 in comparison with cellulose and hemicellulose in a packed bed system [45]. The reason is that cellulose appeared more OH and C-O compounds and hemicellulose contained higher C=O organic compounds, while lignin had higher aromatic rings and O-CH_3 functional groups [45]. The gas analysis revealed CO to be the main compound present in both pyrolysis gases at 500 ºC (32.6 and 29.5 vol% for SB and OH, respectively). The reason might be the decarbonylation and decarboxylation reactions, increasing the amount of CO [63]. SB at 450 ºC and OH at 500 ºC generated the syngas with better calorific values (15.9 and 17.3 MJ/kg) due to higher H_2 volume (25.7 and 23.1 vol%).

Al Arni [27] used a batch reactor to process SB at 500 ºC through two pyrolysis regimes (fast and slow). For both types of fast and slow pyrolysis, the H_2 volumes (8.7 and 9.6 vol%, respectively) were approximately less than half of the TCR SB run with the same pyrolysis temperature (500 ºC). The reforming unit containing biochar as a catalyst could favour deoxygenation reactions resulting in the production of H_2 and improving the HHV of the pyrolysis gas [44].

Ahmad et al. [46] obtained a syngas with the same HHV (13.8 MJ/kg) with similar experimental conditions (TCR of SB at 400 and 500 ºC as pyrolysis and reforming temperatures). Despite **Table 4** showing a higher H_2 yield (21.5 to 12.1 vol%), the lower percentage of CH_4 (19.5 to 15.6 vol%) and CO (32.8 to 21.2 vol%) found in his work might justify the same calorific value between both studies. The different gas composition among both works may come from the use of diverse SB species with different chemical natures. The quantity of combustible gases and the HHV of these experiments are sufficient to be utilised as a fuel for production of heat and power via CHP engines.

Table 4. SB and OH permanent gas composition at different pyrolysis temperatures (reforming temperature = 500 ºC).

	SB			OH		
Pyrolysis Temperature (ºC)	**400**	**450**	**500**	**400**	**450**	**500**
Component						
H_2 (vol%)	21.5	25.7	19.9	16.5	15.8	23.1
CH_4 (vol%)	15.6	13.5	10.9	11.6	7.0	6.4
CO (vol%)	21.2	20.2	32.6	26.5	25.5	29.5
CO_2 (vol%)	30.5	28.8	23.6	30.1	25.6	21.2
C_XH_Y (vol%)	2.5	2.3	2.7	3.0	2.7	3.4
Non-detectable (vol%)	8.7	9.5	10.3	12.3	23.4	16.4
HHV (MJ/kg)	13.8	15.9	13.4	16.2	15.3	17.3
Density (kg/m^3)	0.90	0.89	0.98	0.91	1.2	0.85

3.5 Char Analysis

Table 5 indicates the ultimate analysis of the biochar, ash content and its HHV. Biochar is mainly composed of fixed carbon and ash, as mentioned before. SB biochar suffered a fluctuation in terms of carbon and energy content when the pyrolysis temperature was increased. The biochar from SB produced at 450, and 500 ºC (pyrolysis and reforming temperatures) was the only one out of this context having a substantially lower carbon value and energy content compared to the rest of the trials. For OH runs, the biochar presented similar chemical composition and calorific value between different pyrolysis temperatures.

The SB biochar at 400 ºC contains the highest calorific value (29.7 MJ/kg) attributed to the highest carbon content (79.6 wt%). Inversely, SB biochar at 450 ºC is the less energetic (24.9 MJ/kg) having the lowest carbon value (70.3 wt%). Fixed carbon is the combustible compound of the pyrolysis char raising the HHV [64]. Generally, for the same pyrolysis temperatures, OH char presented less ash and more carbon than the SB char leading to a better HHV. This is a result of the chemical composition of both raw feedstocks, where the OH contains more fixed carbon and less ash compared to SB (**Table 1**). The existence of ash reduces the energy content of the biochar [65].

The present work produced SB biochar (500 ºC) with the HHV between Varma et al. [6] and Lee et al. [66] studies. The first author used fast pyrolysis to process SB at 500 ºC obtaining a char with lower carbon content (66.9 wt%) and subsequently lower energy density (24.3 MJ/kg). However, the second author converted SB via slow pyrolysis at 500 ºC producing biochar with a higher carbon value (85.6 wt%) and HHV (32.8 MJ/kg). Slow pyrolysis involves slower heating rates and longer residence times which promotes aromatisation reactions increasing the C-C bonds and the percentage of fixed carbon in the biochar [67].

Henkel et al. [44] processed SB via intermediate pyrolysis (batch reactor), and the same fluctuation of the SB HHV (from **Table 5**) was observed when the pyrolysis temperature was increased. In the same study, the biochar at 500 ºC demonstrated lower carbon content (71.9 wt%), and calorific value (24.3 MJ/kg) compared to the SB run for the present work at the same pyrolysis temperature. The reforming unit of the TCR

enables a longer residence time of the char causing cracking reactions resulting in final biochar richer in fixed carbon.

In relation to TCR results from the literature review, Ahmad et al. [46] produced SB char at 400 and 500 ºC (pyrolysis and reforming temperature) with higher ash content (30.5 wt%) and lower carbon value (67.9 wt%) and energy density (24.0 MJ/kg). The variance between these results and **Table 5** (for the same parameters) might be due to the different chemical composition of the SB applied. All the biochars from this section contained similar carbon value and energy content when likened to the classic sub-bituminous coal (73.9% carbon and 29.05 MJ/kg energy content) [68]. The only exception is the SB char produced at 450 ºC. The biochar from this set of experiments is energetically interesting to produce heat and power through boilers, gasifiers and furnaces. Moreover, it can also be utilised as a fertiliser, activated carbon and for catalytic upgrading [65, 66, 68-70].

Table 5. SB and OH biochar characterisation at different pyrolysis temperatures (reforming temperature = 500 ºC).

	SB			OH		
Pyrolysis Temperature (ºC)	**400**	**450**	**500**	**400**	**450**	**500**
Ultimate analysis						
C (wt%)	79.6	70.3	77.1	78.2	79.3	79.0
H (wt%)	2.2	1.6	1.5	2.7	2.0	2.3
N (wt%)	0.44	0.39	0.47	1.4	1.1	1.3
S (wt%)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
O (wt%)	2.76	11.61	2.73	2.2	5.8	1.3
Ash (wt%)	15.0	16.1	18.2	15.5	11.8	16.1
HHV (MJ/kg)	29.7	24.9	28.1	29.3	29.2	29.3

3.6 Mass Balance and Energy Yield

The mass balance and the energy yield for the SB and OH experiments are demonstrated in **Figures 3** and **4**. When the pyrolysis temperatures were lower, the production of pyrolysis liquid (bio-oil and aqueous phase/water) and biochar increased. The formation of pyrolysis oil comes from the breakdown of cellulose and hemicellulose at lower temperatures through devolatilisation and depolymerisation reactions [45]. Biochar production is also favoured at low pyrolysis temperatures where charring and cross-linking reactions occur with more intensity [71, 72]. The lowest pyrolysis temperature (400 ºC) resulted in the most significant yields of SB and OH bio-oil and biochar.

At the same time, the gas fraction was maximised due to the degradation of biochar into lighter compounds when submitted to higher temperatures in the pyrolysis reactor. The increment of temperature also promoted other decomposition reactions resulting in less bio-oil and more syngas [44]. The run of SB and OH at 500 ºC (pyrolysis temperature) produced the highest syngas fraction (36.8 wt% and 33.7 wt%, respectively). The gas yields observed in this figure are higher for SB than OH experiments due to the higher water content present in OH feedstock (**Table 1**). More

moisture means less gas produced, which is attributed to the higher removal of water-soluble compounds present in the pyrolysis gas [73].

TCR technology presented a high efficiency in terms of mass balance. The conversion of biomass into valuable products was between 92.8 and 96.8 wt%. In the best experiment, only 3.2 wt% was losses (OH at 450 ºC pyrolysis temperature). The losses might be explained due to errors measuring weights, non-detectable gases by the gas analyser and the remained bio-oil in the cleaning section.

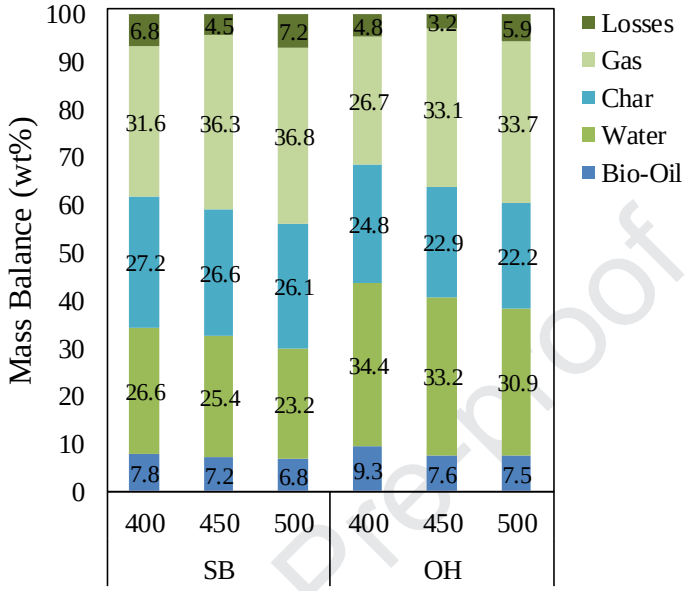

Figure 3. Mass balance of SB and OH trials at different pyrolysis temperatures (reforming temperature = 500 ºC).

It is observed that the OH energy yields for bio-oil are higher than SB for any single pyrolysis temperature (**Figure 4**). This can be explained by the better energy value, and higher oil production found in OH runs (**Table 2** and **Figure 3**). Biochar had the highest energy fraction in all experiments. The best biochar results were achieved with the lowest reforming temperatures for both biomasses, where SB and OH at 400 ºC obtained 49.4 and 45.3%, respectively. Despite the present runs producing more syngas than char, the calorific value of biochar (24.9-29.7 MJ/kg) is significantly higher compared to the pyrolysis gas (13.4-17.3 MJ/kg) which can justify the results from **Figure 4**.

The energy losses were from 7.7 to 11.4%, where the OH trial at 500 ºC was the most efficient one converting 92.3% of the energy from the feedstock into TCR products. In general, SB experiments presented more energy losses than OH, which can be associated with more mass losses demonstrated in **Figure 3**. Furthermore, some pyrolysis liquid could not be extracted from the condensing unit due to the difficulty of collecting all the liquid produced. For that reason, some bio-oil energy was lost and not considered for the energy yields affecting the efficiency of the process.

To sum up, various feedstock (wood, sewage sludge, paper sludge, de-inking sludge, food/market waste and digestate) were processed through TCR plants successfully, and the results have already been published [74]. The TCR produces high-quality products from a wide range of biomass kinds. The energy losses can be minimised by applying efficient isolation and increasing the reactor scale. The last achievement is the commercial TCR system with a 300 kg/h capacity at UMSICHT,

which is the future work of this study [74]. TCR technology proved its efficiency in terms of mass balance and energy yield in this study.

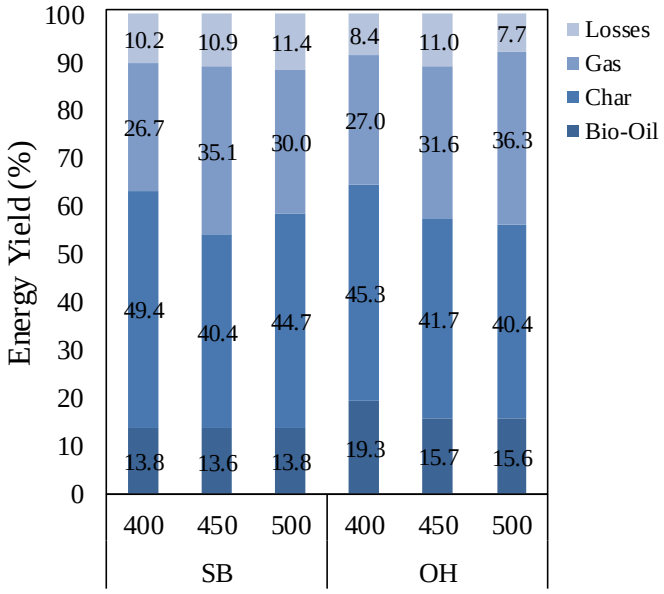

Figure 4. Energy yield of SB and OH trials at different pyrolysis temperatures (reforming temperature = 500 ºC).

4. CONCLUSIONS

In this study, SB and OH were successfully processed using TCR technology in a 2 kg/h continuous pilot-scale reactor. The pyrolysis liquid, char and gas fraction were produced and characterised. Increasing the pyrolysis temperature reduced the oxygen value of the bio-oil and raised its carbon content and the HHV. The total acid number (TAN) of the oils was improved from 32.2 to 25.8 mg KOH/g for SB and from 33.5 to 24.2 mg KOH/g for OH with increasing the pyrolysis temperatures. The increment of pyrolysis temperature improved the viscosity from 47.8 to 23.7 mm^2/s for SB and from 38.1 to 35.3 mm^2/s for OH. The TCR oil would require further upgradings (blending or hydrotreatment) before its application in vehicle engines. The aqueous phase of TCR liquid can be used to improve the TCR hydrogen content for the hydrotreatment process. The HHV of SB and OH biogas did not change significantly with increasing the pyrolysis temperatures. The OH biochar presented similar carbon content and calorific value, but SB biochar did not behave similarly with increasing the pyrolysis temperatures. The highest energy density of the biogas and biochar was 17.3 and 29.7 MJ/Kg respectively, which indicates the potential for generation of heat and power through CHP engines. For the mass balance, the increase of pyrolysis temperature produced more syngas and less bio-oil and char. From 92.8 to 96.8 wt% of the feedstock was converted into valuable TCR products. The energy losses represented between 7.7 and 11.4% of the total energy yield and these can be minimised by applying efficient isolation and increasing the reactor scale. TCR technology proved its efficiency in terms of mass balance and energy yield in this study. Overall, TCR was shown to be a promising future route for the valorisation of lignocellulosic biomass in order to produce energy vectors.

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Valorisation of lignocellulosic biomass investigating different pyrolysis temperatures

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Highlights:

- Sugarcane bagasse (SB) and oat hulls (OH) were successfully converted into valuable products (bio-liquid, syngas, and biochar) using the TCR reactor.
- The fuel properties of the TCR oil improved with the increment of the pyrolysis temperature (higher HHV and lower water, acidity, viscosity and density content).
- TCR technology proved its efficiency in terms of mass balance and energy yield.
- The chemical properties of the TCR products showed the potential to be used as energy vectors.